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Abstract: This study evaluated the effect of air-particle abrasion protocols on the biaxial flexural strength, surface characteristics and phase transformation of zirconia after cyclic loading. Disc-shaped zirconia specimens (Ø: 15mm, thickness: 1.2mm) (N=32) were submitted to one of the air-particle abrasion protocols (n=8 per group): (a) 50µm Al₂O₃ particles, (b) 110µm Al₂O₃ particles coated with silica (Rocatec Plus), (c) 30µm Al₂O₃ particles coated with silica (CoJet Sand) for 20s at 2.8bar pressure. Control group received no air-abrasion. All specimens were initially cyclic loaded (×20,000, 50N, 1Hz) in water at 37°C and then subjected to biaxial flexural strength testing where the conditioned surface was under tension. Zirconia surfaces were characterized and roughness was measured with 3D surface profilometer. Phase transformation from tetragonal to monoclinic was determined by Raman spectroscopy. The relative amount of transformed monoclinic zirconia (FM) and transformed zone depth (TZD) were measured using XRD. The data (MPa) were analyzed using ANOVA, Tukey's tests and Weibull modulus (m) were calculated for each group (95% CI). The biaxial flexural strength (MPa) of CoJet treated group (1266.3±158(A)) was not significantly different than that of Rocatec Plus group (1179±216.4(A,B)) but was significantly higher than the other groups (Control: 942.3±74.6(C); 50µm Al₂O₃: 915.2±185.7(B,C)). Weibull modulus was higher for control (m=13.79) than those of other groups (m=4.95, m=5.64, m=9.13 for group a, b and c, respectively). Surface roughness (Ra) was the highest with 50µm Al₂O₃ (0.261µm) than those of other groups (0.15-0.195µm). After all air-abrasion protocols, FM increased (15.02%-19.25%) compared to control group (11.12%). TZD also showed increase after air-abrasion protocols (0.83-1.07µm) compared to control group (0.59µm). Air-abrasion protocols increased the roughness and monoclinic phase but in turn abrasion with 30µm Al₂O₃ particles coated with silica has increased the biaxial flexural strength of the tested zirconia.

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Effect of air-particle abrasion protocols on the biaxial flexural strength, surface characteristics and phase transformation of zirconia after cyclic loading

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ABSTRACT

This study evaluated the effect of air-particle abrasion protocols on the biaxial flexural strength, surface characteristics and phase transformation of zirconia after cyclic loading. Disc-shaped zirconia specimens (\varnothing : 15 mm, thickness: 1.2 mm) (N=32) were submitted to one of the air-particle abrasion protocols (n=8 per group): a) 50 μm Al_2O_3 particles, b) 110 μm Al_2O_3 particles coated with silica (Rocatec Plus), c) 30 μm Al_2O_3 particles coated with silica (CoJet Sand) for 20 s at 2.8 bar pressure. Control group received no air-abrasion. All specimens were initially cyclic loaded (x20.000, 50 N, 1 Hz) in water at 37°C and then subjected to biaxial flexural strength testing where the conditioned surface was under tension. Zirconia surfaces were characterized and roughness was measured with 3D surface profilometer. Phase transformation from tetragonal to monoclinic was determined by Raman spectroscopy. The relative amount of transformed monoclinic zirconia (F_M) and transformed zone depth (TZD) were measured using XRD. The data (MPa) were analyzed using ANOVA, Tukey's tests and Weibull modulus (m) were calculated for each group (95% CI). The biaxial flexural strength (MPa) of CoJet treated group (1266.3 ± 158^A) was not significantly different than that of Rocatec Plus group ($1179 \pm 216.4^{A,B}$) but was significantly higher than the other groups (Control: 942.3 ± 74.6^C ; 50 μm Al_2O_3 : $915.2 \pm 185.7^{B,C}$). Weibull modulus was higher for control ($m=13.79$) than those of other groups ($m=4.95$, $m=5.64$, $m=9.13$ for group a, b and c, respectively). Surface roughness (R_a) was the highest with 50 μm Al_2O_3 (0.261 μm) than those of other groups (0.15-0.195 μm). After all air-abrasion protocols, F_M increased (15.02-19.25%) compared to control group (11.12%). TZD also showed increase after air-abrasion protocols (0.83-1.07 μm) compared to control group (0.59 μm). Air-abrasion protocols increased the roughness and monoclinic phase but in turn abrasion with 30 μm Al_2O_3 particles coated with silica has increased the biaxial flexural strength of the tested zirconia.

Keywords: Air-abrasion; Biaxial flexural strength; Silica coating; Y-TZP; Zirconia

1. Introduction

Currently, Yttria-stabilized tetragonal zirconia polycrystal (hereon: zirconia) is the most studied ceramic, mainly due to its high modulus of elasticity (White et al., 2005), wear resistance (Tsukamoto et al., 2008), strength and most importantly, its toughness (Guazzato et al., 2004a). These properties enabled zirconia to be milled through CAD/CAM procedures. Toughness of zirconia is related to capacity of tolerating damage and phase transformation where the tetragonal phase is transformed into the monoclinic phase (Kosmac et al., 1999; Guazzato et al., 2005). During this transformation, the energy absorbed by the zirconia matrix in the vicinity of the propagating crack is consumed by the tetragonal (*t*) grains to transform into a monoclinic (*m*) symmetry that is accompanied by ~ 3-4% volume expansion. This volume expansion hinders crack propagation by means of compressive stress (Kosmac et al., 1999; Guazzato et al., 2005).

In dentistry, zirconia is used as a framework material for single crowns and fixed dental prosthesis (FDPs). With the awareness in tooth preservation and the advances in adhesive dentistry, zirconia is also indicated for resin-bonded FDPs where the restoration is adhered on the tooth surface with no or minimal preparations. The survival of such resin-bonded FDPs relies on the durable adhesion of the resin cement both to the zirconia and the tooth surface. As such, surface conditioning of ceramics prior to cementation has become a common procedure. Unfortunately, zirconia in particular is an acid-resistant ceramic. Thus, it is not sensitive to topographic changes by acid etching in order to achieve adequate micromechanical retention (Kern and Wegner, 1998; Özcan and Vallittu, 2003; Kern, 2009; Thompson et al., 2011). In order to compensate for this, adhesive cements containing functional monomers, air-abrasion by means of alumina or with silica coated alumina particles, has been suggested to clean the zirconia surface and promote adhesion of the resin cements (Kern, 2009). Silica-modified particle deposition is chemically more reactive to the resin as they require application of silane coupling agents promoting wettability of the resin, the so-called tribochemical silica coating (Guggenberger, 1989). Against its advantages, while increasing the surface roughness of a zirconia (Della Bona et al., 2007), air-particle abrasion may cause flaws and defects on

zirconia (Zhang et al., 2004, 2005, 2006). Despite the phase transformation and compressive stresses that could prevent crack growth, its strength decreases.

Zirconia is much stronger under monotonic loading than cyclic loading (Morena et al., 1986; Itinoche et al., 2006; Studart et al., 2007a, 2007b). Under monotonic loading, the ceramics simply fail due to surface cone crack growth, whereas cycling loading causes both accumulated plastic damage and phase transformation (Vult von Steyern et al., 2006; Oilo et al., 2009). Moreover, it has been shown that under cycling loading in a wet medium, the crack propagation velocity increases (De Aza et al., 2002; Zhou et al., 2007; Huang et al., 2008). There have been some concerns regarding the application of air-abrasion protocols on the long-term behaviour of zirconia (Kosmac et al., 1999, 2000; Zhang et al., 2004, 2005, 2006).

Abrasives deposited on zirconia surfaces in these studies were of aluminium trioxide (Al_2O_3) with average particle size ranging between 50 to 250 μm in size (Özcan et al., 1998). Alumina particles coated with silica (Rocatec Plus) through the sol gel processes with average particle size up to 110 μm , have been initially introduced for conditioning metal or ceramic surfaces by the dental technicians at the laboratory. Later, the chairside application of tribochemical coating became possible with the development of 30 μm alumina particles coated with silica (CoJet System) (Özcan, 2003). In fact, abrasive particles vary in morphology and it can be anticipated that their impact on the zirconia surface may vary as a function of their morphology and other deposition parameters. Previous studies concentrated mainly on the effect of most commonly used Al_2O_3 particles (Kosmac et al., 1999, 2000; Zhang et al., 2004, 2005, 2006) but to the authors' best knowledge, it is not known whether small size silica coated particles with more favorable morphology may result in less transformation into a monoclinic phase or not. Since surface conditioning of cementation surfaces of zirconia FDPs is a common practice in dentistry, the maintenance of mechanical properties of zirconia after these procedures is essential.

The objectives of this study therefore were to evaluate the effect of air-particle abrasion with different abrasives on the biaxial flexural strength, surface characteristics and phase transformation of a commercial zirconia after cyclic loading in wet conditions. The null hypothesis tested was that air-particle abrasion protocols would neither influence the flexural strength nor the phase transformation of zirconia.

2. Materials and methods

2.1 *Specimens preparation*

Brands, types, manufacturers and batch numbers of the tested materials are listed in Table 1.

Disc-shaped zirconia specimens (Vita In-Ceram 2000 YZ Cubes, Vita Zahnfabrik, Bad Säckingen, Germany) (\varnothing : 15 mm, thickness: 1.2 mm) (N=32) were obtained from the manufacturer, prepared according to ISO 6872, 1998. The final sintering temperature applied was 1500°C. The specimens were ground finished with 10 μ m diamond paper on both sides by the manufacturer [Kosmac et al., 1981; Pittayachawan et al., 2007]. The thickness and diameter of each specimen were verified by measuring with a digital caliper (Starrett 727, Starrett, Itu, Brazil).

The specimens were air-particle abraded with one of the abrasives (n=8 per group): a) 50 μ m Al₂O₃ particles (Polidental Ltd, São Paulo, Brasil), b) 110 μ m Al₂O₃ particles coated with silica (Rocatec Plus, 3M ESPE, Seefeld, Germany), c) 30 μ m Al₂O₃ particles coated with silica (CoJet Sand, 3M ESPE). The specimens that were not air-abraded acted as the control group.

Particles were deposited on the zirconia surfaces using a chairside air-abrasion device (Dento-Prep, RØNVIG A/S, Daugaard, Denmark) adapted to a special metallic holder (Amaral et al., 2008). The nozzle was perpendicular to the specimen surface. The specimens were air-abraded from a distance of 10 mm for 20 seconds at 2.8 bar pressure. Surface conditioning was performed on the tensile side of the specimen in relation to loading cell during cyclic loading and biaxial flexure strength testing.

2.2 Cyclic loading

All specimens were submitted to mechanical cyclic loading (custom made, Sao Paulo State University, Dental School, Sao Jose dos Campos, Brazil) (Itinoche et al., 2006). The specimens were placed in a metallic base having three balls of 3.2 mm diameter each, equidistant from each other and forming a plane (ISO 6872, 1998). An upper rod with a 1.6 mm diameter tip was fixed on the appliance. Cyclic loading was performed under 50 N for 20.000 times, at a frequency of 1 cycle per second (1 Hz). The loading was performed in aqueous medium and a thermostat in each chamber kept the temperature constant at 37°C.

2.3 Biaxial flexural strength test

After cyclic loading was completed, the specimens were subjected to monotonic biaxial loading to determine the critical load for fracture. The specimen holder for the experimental set up was the same for both cyclic testing and monotonic loading. The load was applied in a Universal Testing Machine (Emic DL 1000, Emic, São José dos Pinhais, Brazil) at a constant speed of 1 mm/mm until fracture occurred.

The biaxial flexural strength (MPa) was calculated using Equations (1-3) according to the guidelines of ISO 6872, 1998:

$$S = -0.2387 \frac{P(X - Y)}{d^2}$$

(Equation 1)

where S is the maximum tensile stress in Pascals, P is the total load causing fracture in Newtons, and d is the specimen thickness at the origin of the fracture, in millimeters.

X and Y were determined as follows:

$$X = (1 + \nu) \ln \left(\frac{r_2}{r_3} \right)^2 + \left[\left(\frac{1 - \nu}{2} \right) \left(\frac{r_2}{r_3} \right)^2 \right]$$

(Equation 2)

$$Y = (1 + \nu) \left[1 + \ln \left(\frac{r_1}{r_3} \right)^2 \right] + (1 - \nu) \left(\frac{r_1}{r_3} \right)^2$$

(Equation 3)

where, ν is Poisson's ratio (0.25); r_1 is the radius of the support circle, in mm, r_2 is the radius of the loaded area, in mm; r_3 is the radius of the specimen, in mm; d is the specimen thickness at the origin of the fracture, in mm.

2.4 Raman spectroscopy

Phase transformation ($t \rightarrow m$) of zirconia after air-particle abrasion, was detected using micro-Raman spectroscopy (RFS 100/S, Bruker Inc, Karlsruhe, Germany) that consists of holographic optics, a single ~1800 groove/mm grating, 0.5 μm spectrometer, and a liquid nitrogen cooled CCD detector (11003330 pixels). The laser (Argon ion, green monochromatic light, 514 nm) was focused through a x100 objective to a 1.5 μm beam diameter and two measurements per specimen were carried out, with 4 measurements of 120 seconds each. The peaks related to the monoclinic phase were at 180 and 190 cm^{-1} , whereas the tetragonal polymorphs were represented by all other bands in the collected spectra (148, 263, 322, 466, 614, 645 cm^{-1}).

2.5 X-Ray diffraction analysis (XRD)

The specimens were analyzed in an X-ray Diffractometer (Philips, PW 1830, Almelo, The Netherlands) using monochromatic Cu-K alpha radiation ($\lambda=1.54060 \text{ \AA}$). Scans were performed at 40 kV, 40 mA, 0.02°/step, with step interval ranging from 20° to 60°, at 1 second per step.

The relative amount of transformed monoclinic zirconia (F_M) (%) on the air-abraded surfaces was determined from the integral intensities of the monoclinic (-111)_M and (111)_M, and the tetragonal (101)_T peaks obtained using XRD, according to the method described by Toraya et al., 1984 using the equations (A and B) bellow:

$$F_M = \frac{1.311 * X_M}{1 + 0.311 * X_M}$$

Equation A

$$X_M = \frac{(-111)_M + (111)_M}{(-111)_M + (111)_M + (101)_T}$$

Equation B

where (-111)_M, $2\theta = 28^\circ$; (111)_M, $2\theta = 31.20^\circ$; (101)_T, $2\theta = 30^\circ$, represent the integrated intensity of the peaks diffracted in the monoclinic planes (-111)_M and (111)_M and in the tetragonal plane (101)_T.

Two measurements were carried out on each specimen to obtain the mean values of F_M . Raman spectroscopy and XRD measurements were performed on the tensile side of the specimens.

2.6 Transformed zone depth (TZD)

The transformed zone depth (TZD) (μm) on the air-abraded surfaces of zirconia was calculated from the relative amounts of the monoclinic phase, assuming that, within the transformed surface layer, all the tetragonal grains have transformed into the monoclinic symmetry, according the Equation C bellow (Kosmac et al., 1981):

$$TZD = \left(\frac{\sin\theta}{2\mu} \right) \left[\ln \left(\frac{1}{1 - FM} \right) \right]$$

Equation C

where, $\theta=15^\circ$ is the angle of reflection; μ ($=0.0642$) is the absorption coefficient and F_M the relative monoclinic fraction obtained from the Raman analysis on the basis of Equations A and B.

2.7 3D optical profilometer and SEM analyses

In order to determine the effect of abrasives on the topography and roughness (R_a) of the ceramic surfaces, the same specimens submitted to F_M and TZD analyses were further analyzed using a 3D optical profilometer (Wyko, Model NT 1100, Veeco, USA). Quantification of the 3D-surface roughness parameters (R_a) was performed using the software (Wyko Vision 32, Veeco) at x20 magnification ($301.3 \times 229.2 \mu\text{m}$).

The morphologies of the abrasive particles tested were evaluated under Scanning Electron Microscopy (SEM) (Carl Zeiss NTS, Oberkochen, Germany) at x500 magnification.

2.8 Statistical analysis

Statistical analysis was performed using Statistix for Windows (Analytical Software Inc., version 8.0, 2003, Tallahassee, FL, USA). Kolmogorov-Smirnov test was applied to evaluate the normal distribution of variables and homogeneity test (Levene test) was used to verify the homogeneity of variance. The means (MPa) of each group were analysed by one-way analysis of variance (ANOVA) and Tukeys test to determine significant differences between the experimental groups. Weibull analysis was performed using Minitab Version 14 (Minitab, State College, PA, USA) software. The Weibull statistic was applied based on the formulation where the cumulative distribution function was equal to:

$$G(x) = 1 - \exp \left\{ - \left(\frac{x - s_0}{s} \right)^m \right\}$$

which corresponds for $s_0=0$ to the following density:

$$g(x) = \frac{m}{s} \left(\frac{x}{s} \right)^{m-1} \exp \left\{ - \left(\frac{x}{s} \right)^m \right\}.$$

P values less than 0.05 were considered to be statistically significant in all tests.

3. Results

Homogeneity test verified the uniformity of the data and that none of the ANOVA assumptions were violated (Fig. 1)

Abrasive types tested during air-particle abrasion protocols showed a significant impact on the biaxial flexural strength (MPa) of the tested zirconia ($p < 0.05$). Mean biaxial flexural strength of CoJet treated group (1266.3 ± 158) was not significantly different than that of Rocatec group (1179 ± 216.4) ($p > 0.05$) but it was significantly higher than the other groups (Control: 942.3 ± 74.6 ; $50 \mu\text{m Al}_2\text{O}_3$: 915.2 ± 185.7) ($p < 0.05$) (Table 2, Fig. 2).

Weibull distribution presented higher shape value for control ($m = 13.79$) than those of other groups ($m = 4.95$, $m = 5.64$, $m = 9.13$ for $50 \mu\text{m Al}_2\text{O}_3$, Rocatec Plus and CoJet, respectively) (Table 3, Fig. 3).

Surface roughness (R_a) was the highest with $50 \mu\text{m Al}_2\text{O}_3$ ($0.261 \mu\text{m}$) than those of other groups (0.15 - $0.195 \mu\text{m}$) (Figs. 4a-d, Table 4).

After all air-abrasion protocols, F_M increased (15.02 - 19.25%) compared to control group (11.12%). TZD also showed increase after air-abrasion protocols (0.83 - $1.07 \mu\text{m}$) compared to control group ($0.59 \mu\text{m}$) (Table 4).

Raman spectroscopy of air-braded surfaces from representative samples revealed traces of monoclinic doublets (180 cm^{-1} and 190 cm^{-1}) in the CoJet specimen, whereas in the other groups, such bands were less visible (Fig. 5). However, the XRD revealed peaks indicating a monoclinic phase in the specimens for all groups, including the control (Figs. 6a-d).

SEM images ($\times 500$) indicated rougher surface of individual Al_2O_3 particles compared to silica coated Al_2O_3 particles in the case of Rocatec Plus and CoJet (Figs. 7a-c).

4. Discussion

Numerous studies have been published regarding the effects of different surface conditioning protocols to achieve better adhesion to zirconia (Kern, 2009). However, data concerning the strength of zirconia after surface conditioning protocols specifically using abrasives are limited (Kosmac et al., 1999, 2000; Zhang et al., 2004, 2005, 2006). Therefore, this study was undertaken to evaluate the effect of deposition of different particle types on the mechanical properties and structure of zirconia. Since the particle type had a significant effect on the biaxial flexural strength and phase transformation results, the null hypothesis could be rejected.

Flexural strength of ceramics could be tested either with three-point test (Guazzato et al., 2005; Papanagiotou et al., 2006), four-point test (Giordano et al., 1995; Thompson, 2000), or biaxial flexural strength tests (piston-on-three-ball) (Guazzato et al., 2004b; Curtis et al., 2006a; Itinche et al., 2006; Yilmaz et al., 2007). Among all these methods, fabrication of specimens for three-point flexural test can introduce defects that may not present the standard clinical conditions (Kelly, 1995). Also, the quality of specimens for this type of test is highly dependent on the superficial finish at the edges (Zeng et al., 1996). It was reported to be impossible to remove all flaws in a ceramic during the production of the specimens (Yilmaz et al., 2007). Since fracture begins at the edges, resistance values show great variation. On the contrary, biaxial flexural strength test does not involve edge chippings or fractures because this area is not subjected directly to the load, producing less variation in the values. For these reasons, in this study biaxial flexural strength test was used.

The results of this current study ranging between 915 and 1266 MPa are higher than those reported earlier (Curtis et al., 2006b), where Lava ceramic (1191 - 1267 MPa) was studied after different protocols of mechanical cycling. In that study, interestingly after aging in water even increased values were found (1308 MPa). Using the same methodology and ceramic material, Pittayachawan et al. (2007) reported lower results (1086 - 1164 MPa). These results are even less than the values obtained from air-abraded groups in this study. On the other hand, Kosmac et al. (1999) studied different surface conditioning methods using 110 μm

Al₂O₃ particles, grinding papers or burs on zirconia and the biaxial flexural strength data ranged from 543 to 1021 MPa. Although ISO standard have been followed, even with the same materials variations could be observed. One reason for the differences in biaxial flexural strength values could be attributed to the variations in sintering temperatures of zirconia tested (Hjerppe et al., 2009). In the clinical situations, the presence of dentin under a zirconia FDP and sealing the two materials with a cement layer may yield to more favorable stress distribution than testing an unsupported disc specimen under flexural load according to ISO norms. The results achieved from this current study or others met the requirements of ADA specifications that recommend a minimum flexural strength value of 100 MPa. Yet, it is still questionable whether this value of flexural strength is sufficient in clinical practice when these ceramics are employed (Itinchoe et al., 2006).

In this study, the specimens were subjected to cyclic loading in water since oral fluids at 37°C together with mechanical stresses could aggravate degradation in strength (Kelly, 1995; Huang et al., 2008). Several previous studies reported a significant reduction in the mechanical resistance of ceramics in aqueous environment when compared to testing in dry environment (Kelly, 1995; Pittayachavan et al., 2007). In the case of feldspathic and alumina-based ceramics, this reduction may reach to 30% (Sherill and O'Brien, 1974). The degradation process in aqueous environment is due to corrosion of the ceramic causing growth of small faults (Morena et al., 1986). This is highly important for estimating clinical failures of ceramic restorations (Chevalier, 2006; Kelly and Denry, 2008; Denry and Kelly, 2008). Cyclic fatigue in water was shown to present a high impact on the lifespan of different zirconia materials yielding to significantly lower results than when mechanical cycling was performed in dry conditions (Studart et al., 2007a; Studart et al., 2007b).

Certainly, depending on the state of the surface, the ageing kinetics will vary since the total amount of transformed zirconia would be higher than that in the surface of the unconstrained material after the same exposure time (Deville et al., 2006). Cyclic loading conditions and protocols vary between studies. In the

present study, 20.000 cycles were carried out under 50 N load at a frequency of 1 Hz. In a similar study, alumina and zirconia ceramic discs were submitted to 20.000 cycles, under the same conditions prior to flexural strength testing (Itinoche et al., 2006). Okutan et al. (2006) practiced 1.200.000 cycles, at 50 N and 1.3 Hz to evaluate the fracture strength of ceramic crowns. Sundh and Sjogren (2006) submitted FDPs with zirconia copings to mechanical cycling for 100.000 cycles at 50 N and noticed that the resistance after fracture ranged between 900 and 1900 N among the groups. Larsson et al. (2007) subjected FDPs to mechanical cycling for 10.000 cycles at 1 Hz under loads ranging between 30 and 300 N. Since the aim of this study was to evaluate the effect of cyclic loading on zirconia without fracturing the specimens prior to flexural tests, it was decided to perform 20.000 cycles with a 50 N load.

Zhang et al. (2004) stated that the strengths of air-abraded zirconia specimens show significant reduction in strength after both dynamic and cyclic tests where the specimens presented large starting flaws. In that study, zirconia specimens were air-abraded using 50 μm Al_2O_3 . Interestingly, in this study cyclic loading in water was not detrimental for the silica coated specimens. In previous studies, duration of deposition of abrasive particles ranged between 5 to 15 seconds at 0.5-4 bar pressure, whereas in this study, particles were deposited for 20 seconds. Moreover, in this study, in contrast to other studies where the specimens were air-abraded free-hand in a non-controlled manner, in this study, deposition parameters were better controlled using a specially designed device. Recently, one study group suggested that air-abrasion at 0.5 bar would still result in favourable adhesion compared to higher pressure levels (Attia and Kern, 2011; Yang et al., 2010). In this study, manufacturer's recommendations of 2.8 bar was applied. Such parameters need to be studied more in depth in future studies.

Studying structural changes in zirconia bring additional information regarding to the changes on zirconia after air-abrasion. Especially, the increase in biaxial flexural strength after the application of 30 μm CoJet sand can be explained by the formation of a protective layer against the residual compressive stress on zirconia due to the phase transformation ($t \rightarrow m$) in the air-abraded (Kosmac et al., 1999; Kosmac et al.,

2000; Guazzato et al., 2005). Indeed, Raman spectroscopy revealed traces of the monoclinic doublet (180 cm^{-1} and 190 cm^{-1}), corresponding to the monoclinic phase, in the CoJet particle treated group, whereas in other groups, such bands were less dominant. Similarly, F_M ranged between 11.12 to 19.25% in all groups, being highest for the CoJet group (19.25%). In previous studies, the effect of this particle type on structural changes of zirconia was not studied but deposition of $110\text{ }\mu\text{m Al}_2\text{O}_3$ at 4 bar, resulted in 12.7 to 15.7% F_M (Kosmac et al., 1999; Kosmac et al., 2000) and $110\text{ }\mu\text{m Al}_2\text{O}_3$ at 5 bar in 9.5%. Again, in these studies deposition durations were 15 seconds at 4 bar. It has to be noted that the control group also presented monoclinic phase of 11.12%. Most probably, tension associated with cyclic loading yielded to this result (Curtis et al., 2006a). Furthermore, TZD of the experimental groups varied from 0.59 to $1.07\text{ }\mu\text{m}$, with the highest values found in the CoJet group ($1.07\text{ }\mu\text{m}$). TZD values correspond to the protective layer against residual compressive stresses that is directly linked with an increase in the mechanical resistance of zirconia. The variation in the values among the studies can be explained by the chemical and structural difference, such as concentration, distribution and type of the oxide stabilizer (Sundh and Sjogren, 2006; Sato et al., 2008) and grain size of zirconia materials (Kosmac et al., 1999; Kosmac et al., 2000).

The biaxial flexural strength results should be coupled with Weibull analysis. All particle types presented lower Weibull modulus as opposed to as-sintered group indicating that air-abrasion decreases reliability of the durability of zirconia. Damage from air-abrasion appears to be equivalent to 1 N indentation pressure (Zhang et al., 2004). Thus, it possibly produces preferential transformation nucleation around scratches, due to elastic/plastic damage from tensile residual stresses (Deville et al., 2006). Deposition of $110\text{ }\mu\text{m Al}_2\text{O}_3$ for 15 seconds at 4 bar was able to remove a layer of $60\text{ }\mu\text{m}$ from a zirconia ceramic (Kosmac et al., 2000). Already during milling procedures, stress produced by diamond burs leave traces in the form of grooves. While these grooves are more regular in shape, the topography after air-abrasion resembles edge-shaped grooves being responsible for strength degradation (Kosmac et al., 2000; Guazzato et al., 2005). According to Weibull analysis results, although reliability of zirconia before air-abrasion was higher than as-sintered

group, the lower m values could be compensated with the increase in the mechanical strength especially after air-abrasion with alumina particles coated with silica (CoJet-Sand and Rocatec Plus). Merely the morphology of the particles being more favorable for the silica coated ones may be responsible for less damage on zirconia. Available clinical studies on the survival of zirconia FDPs up to 55 months and 4 years where the FDPs were cemented after 50 μm Al_2O_3 particles at 0.25 MPa for approximately 10 seconds air abrasion presented failure rates of 7 to 13% as a result of technical problems, with no indication of the negative effect of air-abrasion (Wolfart et al. 2009; Sasse et al., 2012). Long-term clinical observations are required to analyze the influence of the air-particle-abrasion protocols on the longevity of zirconia FDPs.

5. Conclusion

From this study, the following could be concluded:

1. Deposition of 50 μm Al_2O_3 for 20 seconds created more roughness, decreased the biaxial flexural strength and Weibull modulus of the tested zirconia compared to the control group.
2. Deposition of silica coated alumina, with approximately 110 μm or 30 μm particle size, increased the biaxial flexural strength but decreased the Weibull modulus being more favorable for the latter.
3. All abrasive types tested increased the monoclinic level and the transformed zone depth in the zirconia compared to control group.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Captions to tables and figures:

Tables:

Table 1 Brands, types, manufacturers and batch numbers of the tested materials.

Table 2 The mean \pm standard deviations of biaxial flexure strength values (MPa) for the experimental groups. *The same superscripted letters indicate no significant differences (Tukey's test, $\alpha=0.05$).

Table 3 Shape and scale values of Weibull distribution for the biaxial flexural strength for each group (95% CI).

Table 4 Mean values for the relative amount of transformed monoclinic zirconia (F_M), transformed zone depth (TZD) and roughness surface (R_a) for the experimental groups.

Figures:

Fig. 1 Probability plot of residuals (response in MPa) indicating normal distribution by plotting against the predicted values.

Fig. 2 Scatter dot plot and bar graphic of means (\pm SD) of biaxial flexural strength (MPa) values according to air-particle abrasion protocol.

Fig. 3 Weibull probability plot for biaxial flexural strength (MPa) of experimental groups (95% CI).

Figs. 4a-d. 3D graphic representation of the zirconia surfaces for **a)** As-sintered, **b)** Al_2O_3 , **c)** Rocatec Plus and **d)** CoJet abraded specimens. Note the red intensity for Group b presenting the roughest surface.

Fig. 5 Raman spectra of zirconia specimens. The arrow indicates the presence of monoclinic doublet (180 cm^{-1} and 190 cm^{-1}), corresponding to the monoclinic phase.

Figs. 6a-d. XRD analyses of as-received and air-abraded zirconia specimens for all experimental groups. (T) Tetragonal zirconia phase; (M) monoclinic phase.

Figs. 7a-c. Scanning Electron photomicrographs of **a)** Al_2O_3 , **b)** Rocatec Plus and **c)** CoJet particles at x500 magnification. Note the rough surface of individual Al_2O_3 particles compared to silica coated Al_2O_3 particles in b and c.

Tables:

Brand	Type	Manufacturer	Batch number
Vita In-Ceram 2000 YZ Cubes	Y-TZP ceramic	Vita Zahnfabrik, Bad Säckingen, Germany	21970
Rocatec Plus	110 µm alumina particles coated with silica	3M ESPE, Seefeld, Germany	269078
CoJet-Sand	30 µm alumina particles coated with silica	3M ESPE	351794
Aluminium trioxide	50 µm alumina particles	Polidental Ltd., São Paulo, Brasil	20919

Table 1 Brands, types, manufacturers and batch numbers of the tested materials.

Experimental groups	Mean ± SD (MPa)	Coefficient of variation (%)	Minimum	Maximum
CoJet-Sand	1266.3 ± 158 ^A	12.48	521	1090.6
Rocatec Plus	1179 ± 216.4 ^{AB}	18.49	777.6	1417.1
Aluminium trioxide	915.2 ± 185.7 ^{BC}	20.30	521	1090.6
As-sintered	942.3 ± 76.5 ^C	7.92	806.2	1059.2

Table 2 The mean ± standard deviations of biaxial flexure strength values (MPa) for the experimental groups. *The same superscripted letters indicate no significant differences (Tukey's test, α=0.05).

Experimental groups	Shape (<i>m</i>)	Scale (<i>s</i>)	Correction
Aluminium trioxide	4.95	991.14	0.881
Rocatec Plus	5.64	1260.79	0.973
CoJet-Sand	9.13	1328.69	0.834
As-sintered	13.79	975.41	0.981

Table 3 Shape and scale values of Weibull distribution for biaxial flexural strength for each group (95% CI).

Experimental groups	F _M (%)	TZD (μm)	Ra (μm)
CoJet-Sand	19.25	1.07	0.194
Rocatec Plus	15.02	0.83	0.195
Aluminium trioxide	19.08	1.06	0.261
As-sintered	11.12	0.59	0.15

Table 4 Mean values for the relative amount of transformed monoclinic zirconia (F_M), transformed zone depth (TZD) and roughness surface (R_a) for the experimental groups.

Figures:

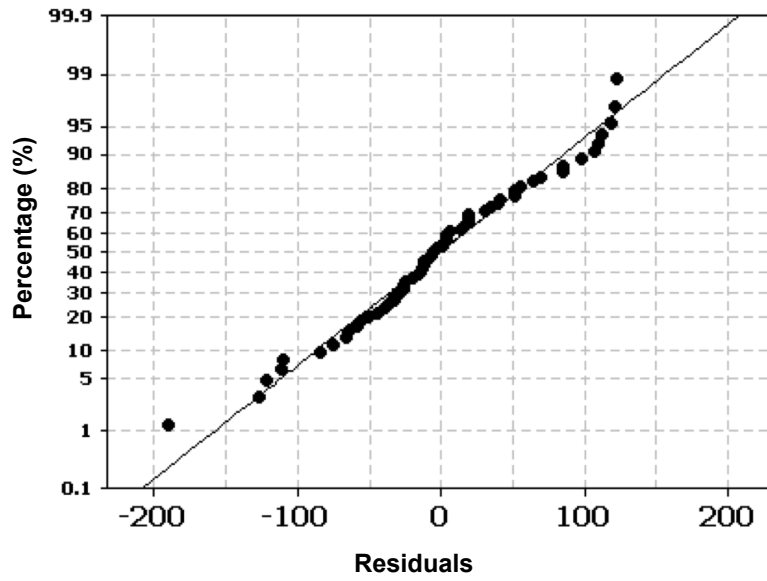


Fig. 1 Probability plot of residuals (response in MPa) indicating normal distribution by plotting against the predicted values.

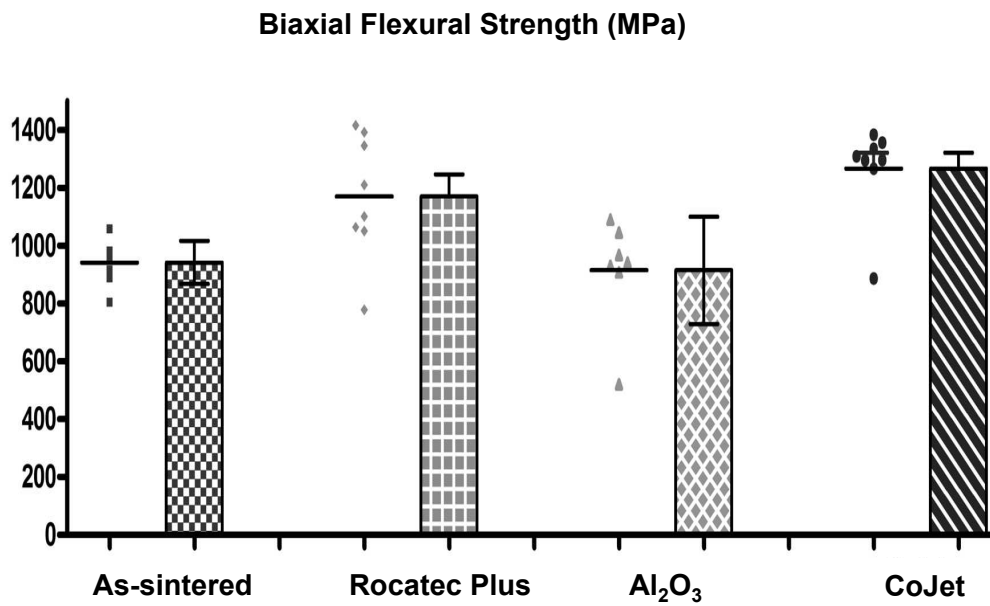


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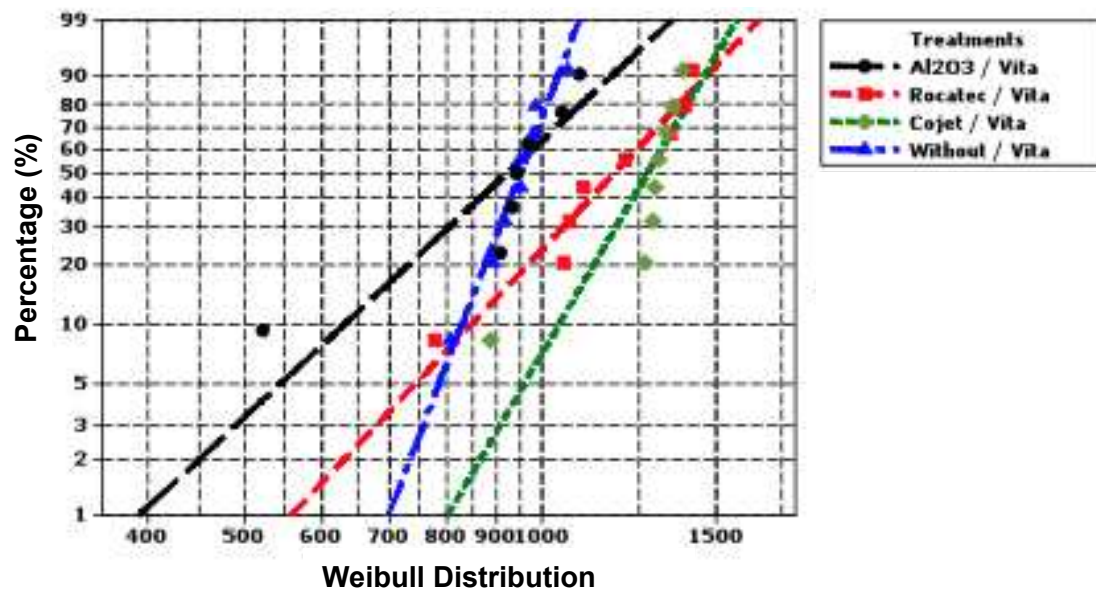
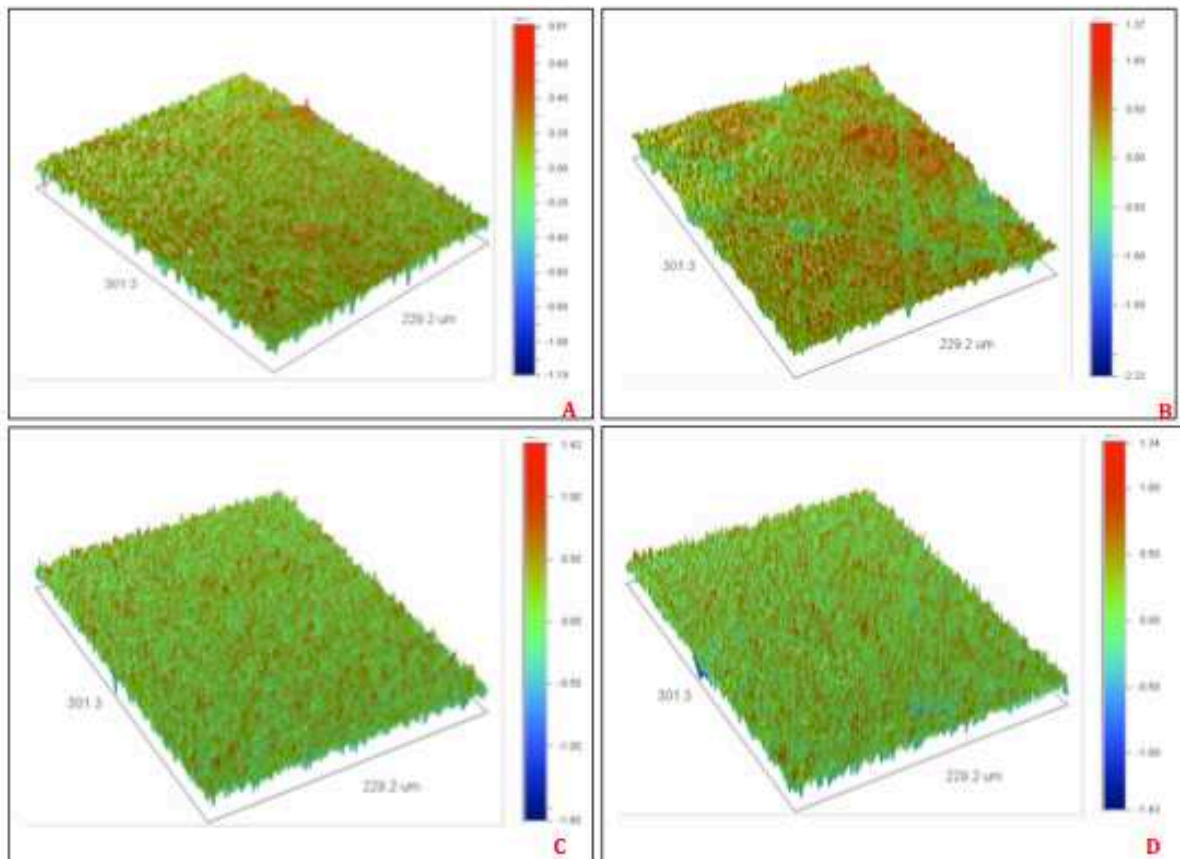


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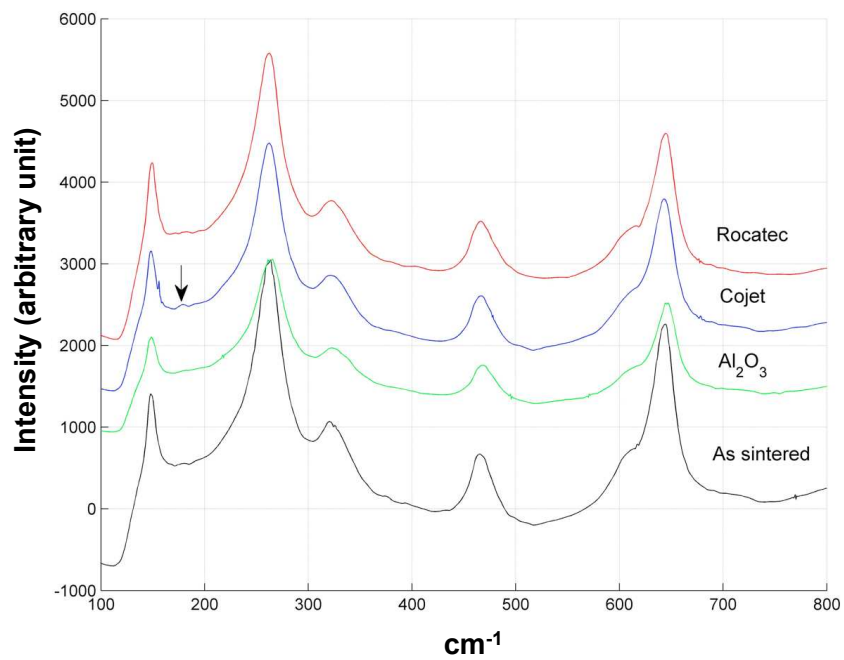
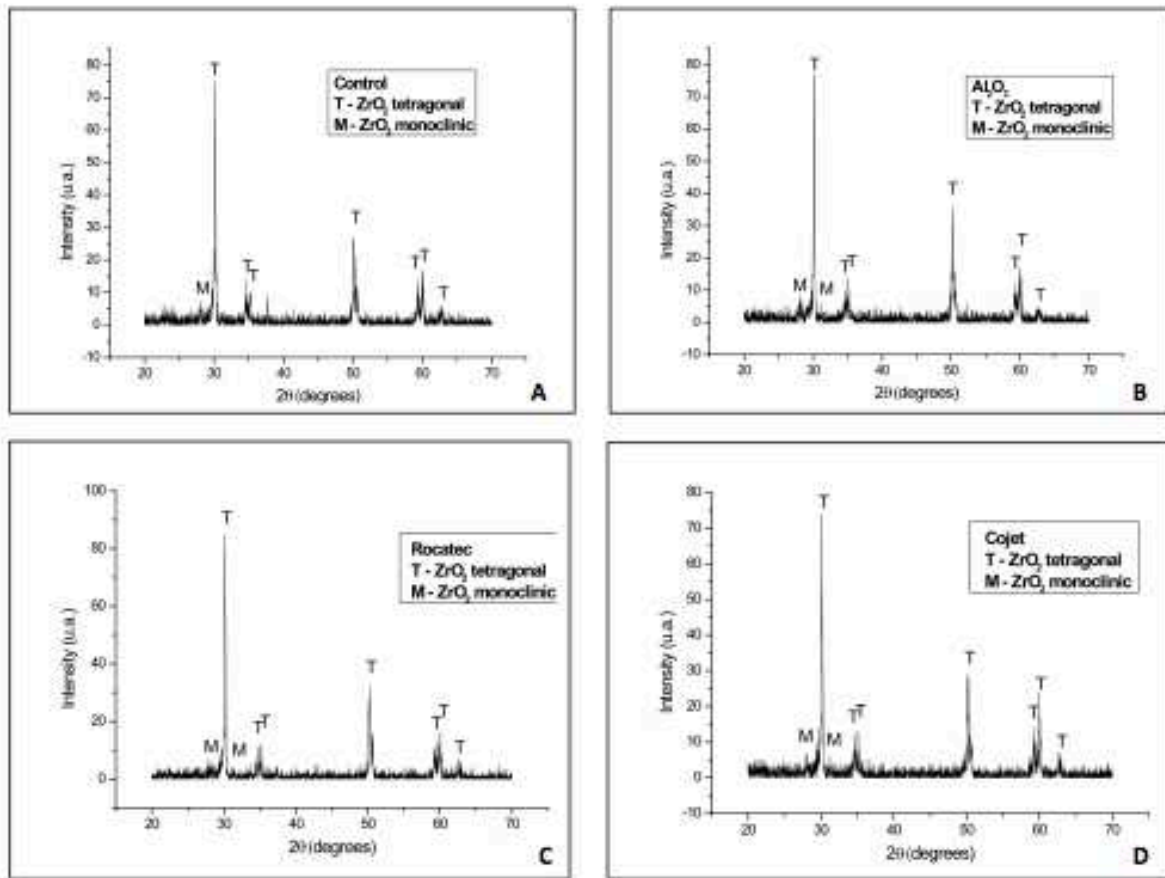
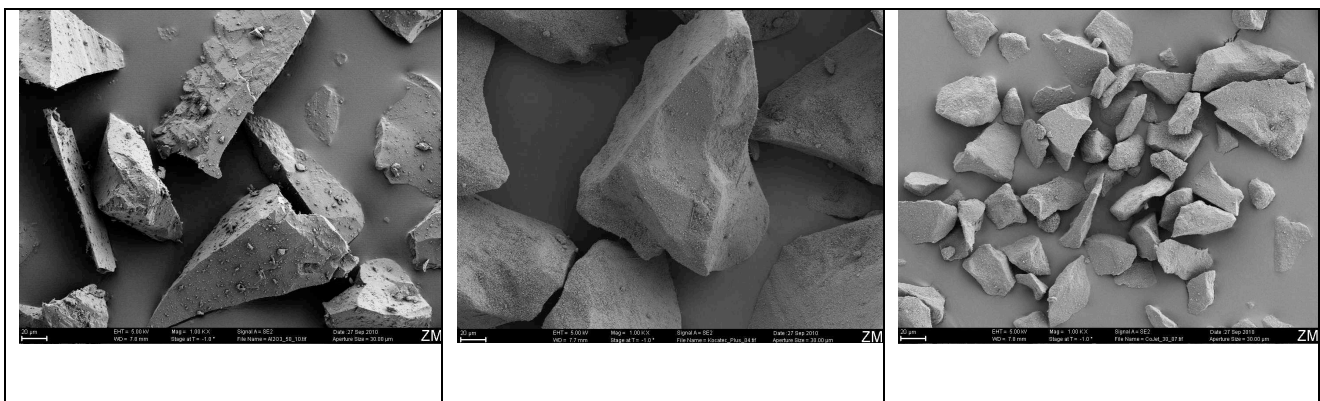


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